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New Substrate/Buffer Layer Compounds for
High Temperature Superconductor
Epitaxial Film Growth

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13. ABSTRACT (Maximum 200 words) A series of compounds in the system A4MeSb012, where A=Ba,Sr and ME=Li,Na and K, were prepared by solid state reaction at elevated temperature. A new form of strontium sodium antimonate (Sr4NaSb3012) was prepared. The compounds that were prepared were characterized with regard to their lattice parameter, density and dielectric properties. Thin films were prepared by pulsed laser ablation deposition from dense targets, and epitaxial relationships identified between YBCO and these compounds.				
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NEW SUBSTRATE/BUFFER LAYER COMPOUNDS FOR HIGH TEMPERATURE SUPERCONDUCTOR EPITAXIAL FILM GROWTH

INTRODUCTION

The best superconducting electronic devices have been fabricated as thin film epitaxial structures deposited on dielectric substrates or buffer layers. To achieve high quality films, dielectric substrates/buffer layers must meet stringent requirements. [1 -5]. Most devices described in the literature have been deposited on lanthanum aluminate (LaAlO_3) or magnesium oxide (MgO) substrates and buffered yttrium stabilized zirconia (YSZ) or sapphire, all of which have some drawbacks. LaAlO_3 has a dielectric constant in the range 22- 24 which means at high frequency (> 12 GHz) device features become unmanageably small. Furthermore this compound is rhombohedral creating difficult device calculations due to its anisotropic dielectric constant. Finally, it undergoes a phase transition resulting in twinning and strain. While MgO has a low dielectric constant (10-12) it provides a poor lattice match to high temperature superconductors (HTSC) resulting in a mismatch of as much as 7%. Sapphire has a very large and anisotropic dielectric constant resulting in very difficult device calculations.

Recently, we have been investigating antimonates with ordered perovskite structures because they have relatively low dielectric loss (10^{-3}) and low isotropic dielectric constants [6,7]. In this paper we report on the deposition of thin film compounds by pulsed laser deposition in the antimonate system $\text{A}_4\text{MeSb}_3\text{O}_{12}$, where A= barium (Ba), strontium (Sr) and Me= lithium (Li), sodium (Na) and potassium (K). The crystal structures of the compounds in the system barium Me antimonate ($\text{Ba}_4\text{MeSb}_3\text{O}_{12}$), where Me=Li and Na, have been previously determined by x-ray and neutron diffraction [8-10]. Both Li and Na compounds are cubic, $\text{Im}\bar{3}\text{m}$ perovskites and exhibit a Me:Sb ordering of 1:3 on octahedral (B) sites. Strontium sodium antimonate ($\text{Sr}_4\text{NaSb}_3\text{O}_{12}$) has been reported to be monoclinic $\text{P}2_1/\text{n}$ as determined from x-ray and neutron diffraction studies [11]. This is in contrast to what we have found.

EXPERIMENTAL

Bulk compounds were prepared by solid state reaction between reagent grade barium carbonate (BaCO_3), strontium carbonate (SrCO_3), lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3) and antimony trioxide (Sb_2O_3) by reacting intimate mixtures of stoichiometric amounts of each. Components were ground together in a mortar, the resulting mixture was pressed into discs and heated to 1100°C (rate= 180°C/hr) for 15 hours in air, cooled to 100°C at the same rate, and removed from the furnace. The disc was reground to a powder with a particle size of $100\mu\text{m}$ or less, pressed into 1-1/4 inch discs between 1/8 and 1/4 inch thick in a steel die, then repressed isostatically at 60000 psi, sintered at $1450\text{-}1600^\circ\text{C}$ for 20-50 hours, cooled to 100°C and removed from the furnace. The discs after sintering were about one inch in diameter. Lattice parameters were obtained from diffractometer scans taken between $15\text{-}155^\circ 2\theta$ using $\text{CuK}\alpha$ radiation ($\lambda=1.5405\text{ \AA}$) or $\text{FeK}\alpha$ ($\lambda=1.93604$) using a least squares fit to the Nelson-Riley [12] function for the last 15 diffraction peaks.

Density measurements were obtained with a helium gas pycnometer on Sintered bulk discs. Earlier investigators prepared some of these compounds by firing samples between 1000 and 1400° C [8--10]. We found that sintering temperatures between 1550-1600° C were required to achieve very dense samples. Such samples were essential for complex dielectric measurements. Experimental densities are compared with x-ray densities in Table 1.

TABLE 1. PROPERTIES of $A_4MeSb_3O_{12}$ COMPOUNDS

COMPOUND	SINTERING TEMP (°C)	LATTICE PARAMETER A		DENSITY (g/cm ³)		DIELECTRIC	
		THIS WORK	LITERATURE	X-ray	Exp.	CONST	LOSS 10 ³
Sr ₄ NaSbO ₁₂	1450	8.180	8.0792 [11] (a=8.0913) (b=8.0871) (c=8.0918) (b=89.953)	5.52	5.60	11.5	9.0
Sr ₄ KSb ₃ O ₁₂	1450	8.23*			6.72	9.0	2.5
Ba ₄ LiSb ₃ O ₁₂	1450	8.221	8.217 [8]	6.65	6.62	16.2	0.5
Ba ₄ NaSb ₃ O ₁₂	1450	8.275	8.273(4) [10]	6.62	6.64	14.4	0.6

*pseudo cubic

Microwave measurements of the real and imaginary parts of the dielectric constant were performed at approximately 9.32 and 10.0 GHz at room temperature. A detailed account of the experimental equipment and procedure may be found elsewhere [7]. The dielectric data for each compound may be found in Table 1. The sintered discs were also employed as targets for deposition of thin films by pulsed laser ablation deposition (PLD). A KrF excimer laser ($\lambda=248$ nm) was employed for deposition using a pulse repetition rate of 10 Hz and a laser fluence of 1-2 J/cm² at the target; other deposition parameters for each sample are given in Table 2.

TABLE 2. DEPOSITION PARAMETERS

COMPOUNDS	OXYGEN PRESSURE (m Torr)	HEATER BLOCK TEMP. (°C)
Sr ₄ NaSb ₃ O ₁₂	80	720
Sr ₄ KSb ₃ O ₁₂	170	800
Ba ₄ LiSb ₃ O ₁₂	170	800
Ba ₄ NaSb ₃ O ₁₂	80	720

RESULTS

All the Ba compounds are cream in color as previously reported [8]. X-ray diffraction patterns were indexed as body-centered cubic consistent with the literature, and lattice parameters are in good agreement with the literature. $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$ is also cream colored. An x-ray diffraction powder pattern was indexed as face-centered cubic. Woodward et al. [13] have described in the series $\text{A}_2\text{M}^{3+}\text{M}^{5+}_6$ face-centered cubic perovskites a subcell based on hkl reflections all even and a supercell based on hkl all odd reflections arising as a consequence of long range order. We observe a similar subcell and supercell in $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$ and, as was observed by Woodward et al., the lattice parameter for the supercell is smaller than that of the subcell. The intensities of the diffraction peaks of the supercell are much weaker than those of the subcell.

Analysis of x-ray diffraction data obtained from films of $\text{A}_4\text{MeSb}_3\text{O}_{12}$ on YBCO (001)/MgO (100) reveals a predominant epitaxial relationship: $\text{A}_4\text{MeSb}_3\text{O}_{12}$ (h00)/YBCO (001)/MgO (100). A second weaker relationship $\text{A}_4\text{MeSb}_3\text{O}_{12}$ (hh0)/YBCO (001)/MgO(100) is also present (see Table 3). Strontium Potassium Antimonate ($\text{Sr}_4\text{KSb}_3\text{O}_{12}$) is not cubic. However, thin films prepared by PLD are highly oriented exhibiting the relationship: $\text{Sr}_4\text{KSb}_3\text{O}_{12}$ (220)/MgO (100). The observed dielectric constant and loss are in the same range as other antimonates previously investigated (see Table 1) [6,7].

TABLE 3. OBSERVED X-RAY REFLECTIONS

STRUCTURE	MgO	YBCO	A4MeSb3O12	INTENSITY
Sr4KSb3O12/MgO			200	very weak
			220	very strong
			222	very weak
	200			weak
			440	medium
			444	very weak
Sr4NaSb3O12/YBCO/MgO		002		weak
			200	weak
		003		medium
			220	very weak
		005		strong
			400	very strong
		006		strong
		007		very weak
Sr4KSb3O12/YBCO/MgO			002	strong
		003		medium
			220	weak
		005		strong
	200			very strong
			400	very strong
		006		strong
			422	very weak
		007		weak
			442/600	very weak
		009		very weak
		0010		very weak
			800	very weak
Ba4NaSb3O12/YBCO/MgO			110	weak
		002		medium
			200	medium
		003		medium
			200	weak
		005		medium
	200			very strong
			400	strong
		006		medium
		007		medium
		008		very weak
		009		very weak
Ba4LiSb3O12/YBCO/MgO			200	very weak
			300	weak
		111		very weak
			211	very weak
			220	very weak
		005		strong
			400	very strong
	200			very strong
		006		very strong
		007		medium
		008		weak
		009		weak
			622	weak
		0010		weak
		0011		weak

CONCLUSION

If we consider the tolerance factor, $t = (r_A + r_O) / \sqrt{2} (r_B + r_O)$ where r_A and r_B are the radii of the A and B ions (Shannon and Prewitt crystal radii [14]), for all Ba compounds the ratios are about 1 or greater and between 1.0 and 0.9 for the Sr compounds. One might expect distortion from the cubic system but this does not occur until the alkali metal K. The difference in charge between B site ions is 4+, which is a major driving force for ordering as predicted by Galasso et al. [15]. $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$ crystallizes as a monoclinic phase when prepared between 680 and 94° C. Analysis of x-ray data suggests a cubic body-centered structure [11]. Why then does $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$ crystallize with a cubic face-centered structure when prepared above 1450° C, while barium sodium antimonate ($\text{Ba}_4\text{NaSb}_3\text{O}_{12}$), prepared at the same temperature, crystallizes with a body-centered structure similar to the low temperature form of $\text{Sr}_4\text{NaSb}_3\text{O}_{12}$? An obvious explanation arises from a comparison of the size of Ba^{2+} and Sr^{2+} . Since Sr^{2+} is smaller, the B-B distances are more compressed, changing the ordering energy of Me^{1+} and Sb^{5+} , which produces the difference.

$\text{A}_4\text{MeSb}_3\text{O}_{12}$ compounds provide one advantage over other antimonates previously investigated. While $\text{Sr}_2\text{GaSbO}_6$ and $\text{Sr}_2\text{ScSbO}_6$ provided a better lattice match to YBCO, $\text{A}_4\text{NaSb}_3\text{O}_{12}$ compounds afford better chemistry. In either case, diffusion of B site ions across the substrate/buffer layer interface will lead to substitution in YBCO films. In the case of Sc and Ga this results in a reduction in T_c when they substitute for Cu. However, Li, Na and K have all been reported to have no effect or increase on T_c and J_c , when present in small concentrations, depending upon the substituent site [16-19]. The use of $\text{A}_4\text{MeSb}_3\text{O}_{12}$ compounds as substrates/buffers turns a detriment, diffusion of ions across an interface, into an advantage.

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